

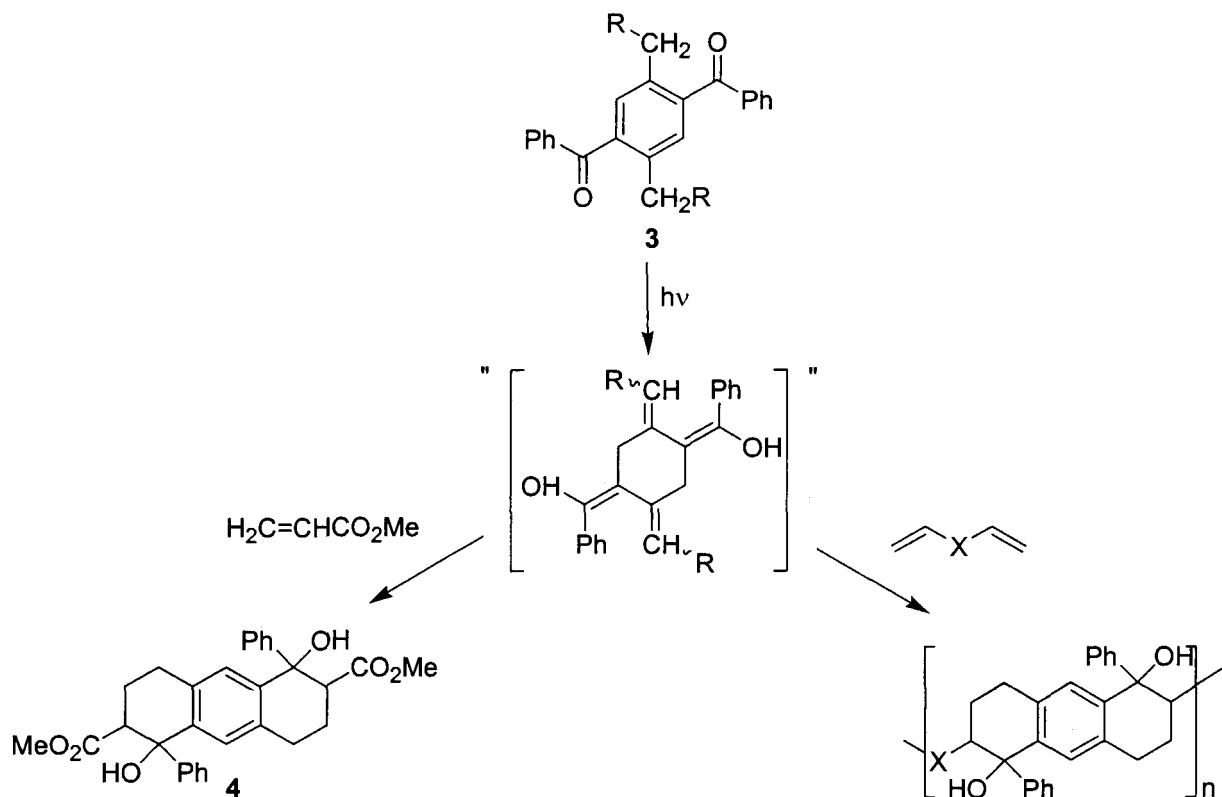
Diels-Alder Trapping of Photochemically Generated *o*-Xylenols – Application in the Synthesis of Novel Organic Molecules and Polymers

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Introduction

Excited state intramolecular hydrogen abstractions are some of the best studied processes in organic photochemistry¹. Among this class of reactions, the photoenolization of *o*-methylphenyl ketones has received a considerable amount of attention from both a mechanistic and a synthetic perspective^{2,3}. This reaction, which typically occurs from the (n,π^*)³, involves abstraction of an *o*-methyl hydrogen by the carbonyl oxygen to afford a triplet 1,4-biradical (Scheme 1). Decay of this biradical to the ground state affords two singlet biradicals, which are resonance equivalents of two *o*-hydroxy quinodimethanes or *o*-xylenols. These *o*-xylenols are designated *E*- and *Z*- to denote the relative positions of the –OH and *exo*-methylene groups. The *Z*-xylenol is short lived (a nanosecond or less, depending upon the solvent) and reverts to ketone via a 1,5-hydrogen shift⁴. However, the *E*-xylenol cannot undergo this 1,5-hydrogen shift and has a significantly longer lifetime, up to microseconds in hydrogen bonding solvents. This is long enough to enable it to undergo chemistry – principally intramolecular cyclization to benzocyclobutanols or Diels-Alder cycloadditions.

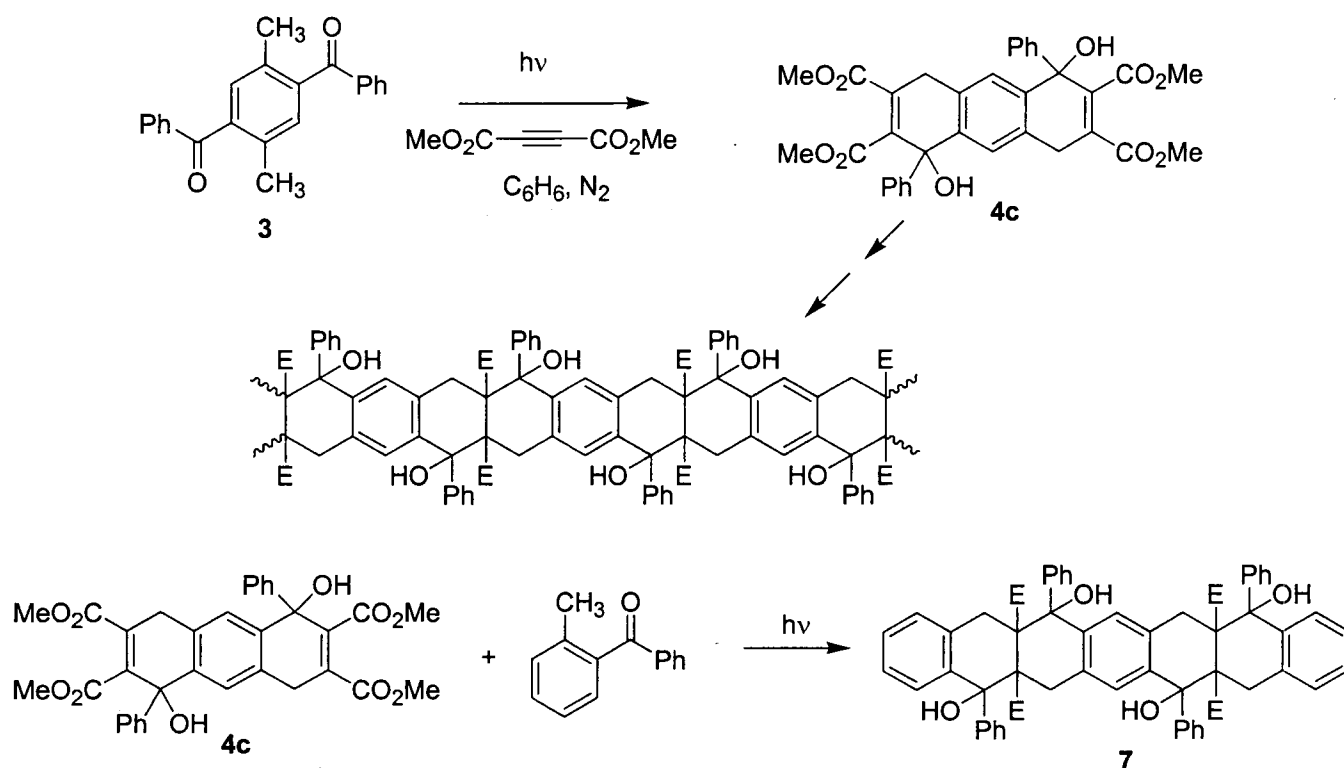
In 1961, Yang and Rivas reported that *o*-xylenols generated by irradiation of either *o*-methylbenzophenone, **1a**, or *o*-benzylbenzophenone, **1b**, could be trapped via a Diels-Alder cycloaddition with dimethyl acetylenedicarboxylate to afford the corresponding tetralin derivatives, **2**, in reasonable yields (Scheme 1)⁵. Since this early report, the Diels-Alder trapping of *o*-xylenols has been used extensively in the construction of fused 6-membered ring systems^{3,6}. With a few exceptions⁷, these



Scheme 2. Generation and trapping of bis(*o*-xylenol)s from 2,5-dibenzoyl-*p*-xylenes.

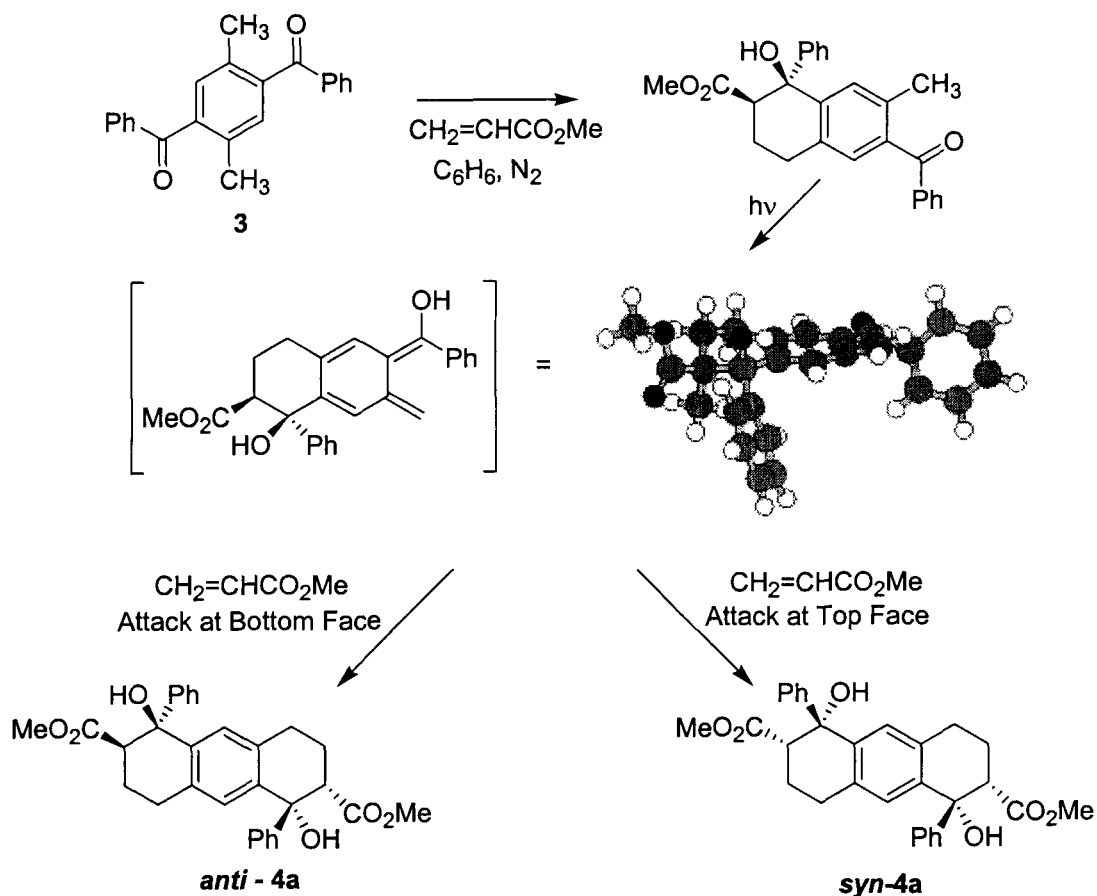
Trapping of o-Xyenols Generated from 2,5-Dibenzoyl-p-xylenes

Our first entry into this chemistry dealt with the use of substituted 2,5-diaryoyl-*p*-xylenes, **3**, as bis(*o*-xylenol) equivalents. These diketones are readily prepared by the reaction of the corresponding substituted arylmagnesium bromide with 2,5-dimethyl terephthalonitrile followed by acid hydrolysis of the resulting diimine. Irradiation of benzene solutions of **3** and a slight stoichiometric excess of representative dienophiles afforded the corresponding 1,5-dihydroxy-1,5-diaryloctahydroanthracenes, **4**, in high yield⁸ (Scheme 3). These octahydroanthracenes can be converted into 1,5-diphenylanthracenes, **6**, in two steps, catalyzed dehydration followed by dehydrogenation/aromatization with DDQ.



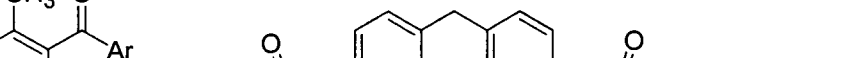
Scheme 4. Polymer formation from trapping of bis(*o*-xenol)s with dimethyl acetylenedicarboxylate.

Diels-Alder trapping of *o*-xenols generated from diketone **3** produced two isomeric bisadducts – one in which the two $-\text{OH}$ groups are on the same face of the molecule, *syn*, and one in which they are on opposite faces, *anti* (Scheme 5). The structure of both isomers was confirmed by a combination of spectroscopy, X-ray crystallography, and chemical derivatization. The basic stereochemical and regiochemical outcome of this cycloaddition follows that observed by Block and Stevenson for *o*-xenols derived from *o*-methylbenzophenone.⁹ Hydrogen bonding between the *o*-xenol $-\text{OH}$ and the ester group on the dienophile directs the cycloaddition process and results exclusively in bisadducts in which the $-\text{OH}$ and ester are on vicinal carbons and are *cis* to each other.

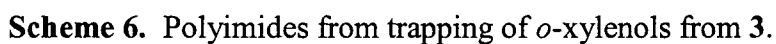


Scheme 5. Stereochemical and regiochemical outcome for trapping of *o*-xylenols from **3**.

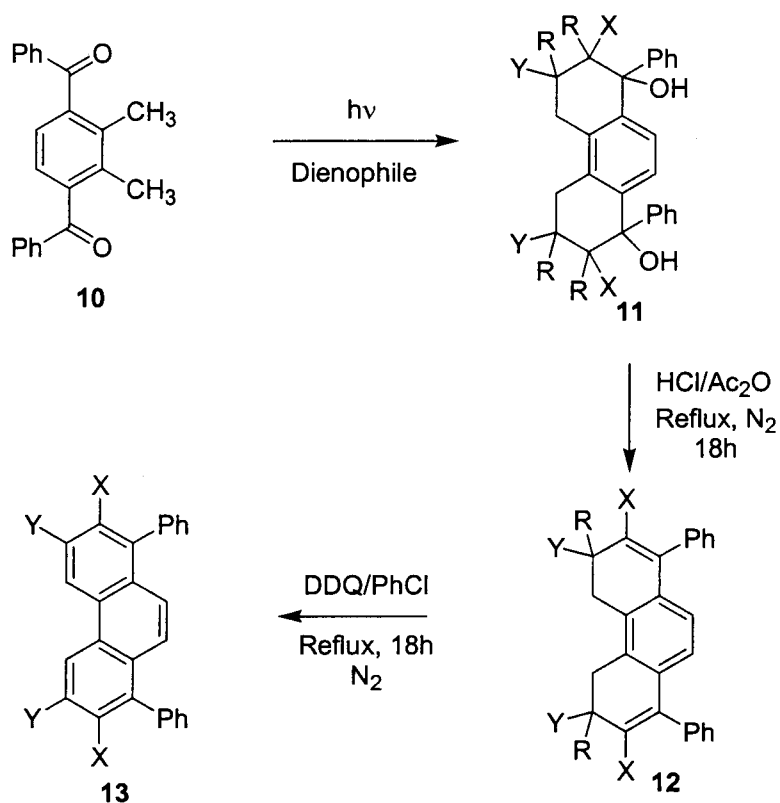
The melting point of **anti-4a** is more than 150°C higher than that of **syn-4a** (295-296°C vs. 130-132°C). This large difference in melting points can be explained by the differences in modes of self-assembly between the two diastereomers. Intermolecular hydrogen bonding between *syn* bisadducts results in the formation of dimeric structures, since both -OH groups are on the same face of the molecule. However, the -OH groups of the *anti* bisadduct are on opposite faces and intermolecular hydrogen bonding produces columnar structures in which the bisadducts are directly superimposed on top of each other. A top-down view of the X-ray crystal structure of stacks formed from **anti-4a** (Figure 1) shows the perfect alignment of the phenyl substituents on each bisadduct. These pendant phenyls are separated by about 4 Å (edge to edge distance). In essence, these columnar structures could serve as molecular scaffolds upon which certain functional groups could be attached to give materials with various properties such as



$$\text{Ar} = \text{Ph}, 4\text{-(OC}_{12}\text{H}_{25})\text{Ph}$$



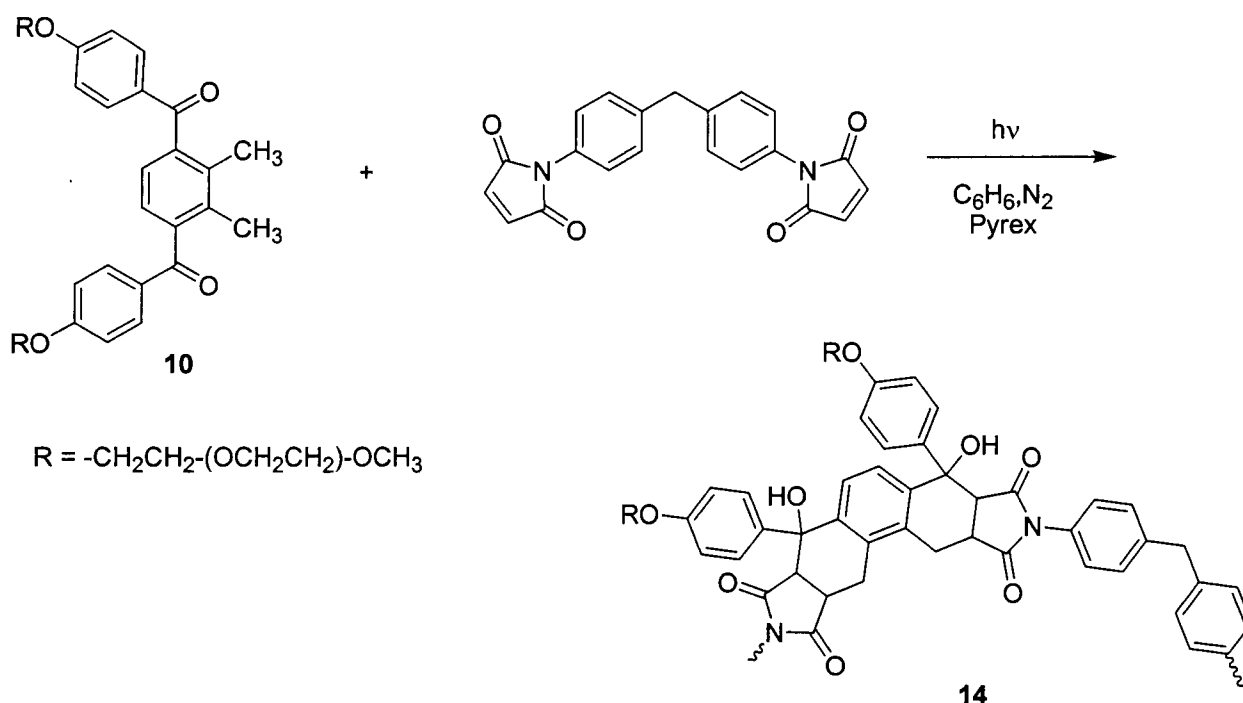
Similarly, polyesters **9** can be prepared both in solution (cyclohexanone or benzene) and in thin films by irradiation of diketones and a variety of commercially available bisacrylates having alkyl or oligo- (ethylene oxide) or (propylene oxide) spacing groups¹¹. As expected, these have lower glass transition temperatures (<160°C) than the polyimides described above. However the resulting films are significantly more



Dienophile	X	Y	R
Methyl acrylate	CO_2Me	H	H
Dimethyl fumarate	CO_2Me	CO_2Me	H
Dimethyl acetylenedicarboxylate	CO_2Me	CO_2Me	--
N-Phenylmaleimide	CO-N(Ph)-CO		H

Scheme 7. Bisadducts from trapping of *o*-xenylenols from 11.

Both *syn* and *anti* bisadducts are formed in this system as well, however, the *anti* isomer is formed in slightly higher yield than the *syn* – formation of *anti* 11a is favored 3:2 over *anti*-11a. This is in sharp contrast to bisadducts formed from 2,5-dibenzoyl-*p*-xylene, 3, where the *syn* isomer is the preferred photoproduct. The solubility behavior of bisadducts formed from these two isomeric diketones is also different. *Anti*-bisadducts produced from diketone 3, were insoluble in methanol and could be readily separated from photoproduct mixture by trituration. However, the *syn* bisadducts formed from diketone 10 were insoluble in methanol while the *anti* isomer was soluble. This suggests that *syn*- and *anti*- 11 may form different structures in the crystal than do *syn*- and *anti*- 4. X-ray crystallographic studies are underway to test this hypothesis.



Scheme 10. Polyimides from trapping of *o*-xlenols from diketone **10**.

Summary

Bis(*o*-xlenol) equivalents are useful synthetic intermediates in the construction of polymers and hydroxyl substituted organic molecules which can organize by hydrogen bonded self-assembly into unique supramolecular structures. These polymers and supramolecular materials have potential use as coatings and thin films in aerospace, electronic and biomedical applications.

Acknowledgements

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10. Meador, M.A.B.; Meador, M.A.; Williams, L.L.; Scheiman, D.A.
Macromolecules **1996**, *29*, 8983.
 11. Meador, M.A.; "Polyesters by Photochemical Cyclopolymerization", US Patent No. 6,486,230 B1, November 26, 2002.
 12. Meador, M.A. and Ilhan, U.F.; *unpublished results*